



## D E C L A R A T I O N

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[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] ELECTROLYTE MEMBRANE-ELECTRODE  
ASSEMBLY FOR FUEL CELL AND METHOD OF OPERATING FUEL CELL USING  
THE SAME

[CLAIMS]

[Claim 1] An electrolyte membrane-electrode assembly  
for fuel cells, comprising a polymer electrolyte membrane and  
a pair of electrodes with said polymer electrolyte membrane  
interposed therebetween, wherein

each of said electrodes comprises a catalyst layer  
in contact with said polymer electrolyte membrane and a gas  
diffusion layer which has a water repellent layer in contact  
with said catalyst layer,

the base material of said gas diffusion layer is  
made of a carbon fiber woven fabric, and

the relationship:  $1/1500 \leq (10/W-Y)(10/Z-X)/XY \leq 1/5$   
is satisfied when said carbon fiber woven fabric has a warp  
density of Z threads/cm, a weft density of W threads/cm, a  
warp thickness of X mm and a weft thickness of Y mm.

[Claim 2] The electrolyte membrane-electrode  
assembly for fuel cells in accordance with claim 1, wherein  
said carbon fiber woven fabric has a thickness in the range of  
0.05 mm to 0.3 mm.

[Claim 3] The electrolyte membrane-electrode

assembly for fuel cells in accordance with claim 1 or 2, wherein said carbon fiber woven fabric has a density in the range of 0.32 g/cc to 0.42 g/cc.

[Claim 4] The electrolyte membrane-electrode assembly for fuel cells in accordance with any of claims 1 to 3, wherein one of said warp density and said weft density of said carbon fiber woven fabric is in the range of 16 threads/cm to 45 threads/cm, and the other of said two densities is in the range of 12 threads/cm to 40 threads/cm.

[Claim 5] A method of operating a fuel cell which comprises the electrolyte membrane-electrode assembly for fuel cells in accordance with any of claims 1 to 4, and generates electric power by providing a supply of a humidified fuel gas to the anode and a supply of a humidified oxidant gas to the cathode, comprising a step of:

controlling the dew point of said fuel gas and the dew point of said oxidant gas to temperatures equivalent to, or 5 °C or less lower than, the temperature of said electrolyte membrane-electrode assembly in operation.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to an electrolyte membrane-electrode assembly for polymer electrolyte fuel cells, using a proton conductive polymer electrolyte membrane, and a method of operating a fuel cell using this electrolyte

membrane-electrode assembly.

[0002]

[Prior Art]

An electrolyte membrane-electrode assembly (hereinafter referred to as MEA) for a polymer electrolyte fuel cell (hereinafter referred to as PEFC) generally comprises a polymer electrolyte membrane and a pair of electrodes with the polymer electrolyte membrane interposed therebetween. Each of the electrodes comprises a catalyst layer in contact with the polymer electrolyte membrane, and a gas diffusion layer having a water repellent layer in contact with the catalyst layer. The MEA is supported from both sides thereof by separator plates comprising gas flow channels and, together with sealants for preventing gas leakage, cramped by a constant pressure to constitute a unit cell of a PEFC.

[0003]

In the separator plate formed are grooves (gas flow channels) from an inlet to an outlet for a reaction gas (fuel gas or oxidant gas), and the reaction gas is arranged to flow in the gas flowing channels. It is required that the gas diffusion layer function to diffuse a reaction gas supplied through the gas flow channels, to be supplied throughout the catalyst layer. It is also important that the gas diffusion layer function to discharge excess water in order to prevent water, produced in the cathode-side catalyst layer by the reaction of the PEFC in operation, from impairing the

diffusibility of the reaction gas. Namely, it is important that the gas diffusion layer function to prevent produced water from clogging up the micropores within the gas diffusion layer, and to make the produced water pass therethrough so that it may smoothly reach the gas flowing channels in the separator plate. The gas diffusion layer is in contact with convex portions (ribs), formed on each side of the respective gas flowing channels in the separator plate, to be electrically connected to the separator plate, and it hence serves to conduct a current, generated at the MEA, to the separator plate.

[0004]

A water repellent layer is usually formed on the catalyst-layer-contacting-side of the gas diffusion layer, and a fluorocarbon resin is used as the water repellent material of the water repellent layer. The water repellent layer comprises an electron conductive material such as carbon, together with the water repellent material. In the conventional commonly-used technique, a base material of a gas diffusion layer has a porous structure for securing gas diffusibility, a water repellent layer is formed on the gas diffusion layer for controlling water penetrability, and further, an electron conductive material such as carbon fiber, metal fiber or the like is used as the gas diffusion layer base material for securing electron conductivity. As a typical gas diffusion layer base material used has been carbon

paper, carbon felt, carbon fiber woven fabric, or the like.

[0005]

There are differences in those characteristics due to differences in the basis weight and thickness of carbon paper or carbon felt. Since carbon paper, as well as carbon felt, is composed of carbon fibers arranged at random, however, there are not much differences in gas diffusibility and water permeability due to a difference in fiber arrangement. Since a carbon fiber woven fabric is woven such that carbon fibers are regularly arranged, on the other hand, the weave of the fabric is another important dominant factor of the above characteristics besides the basis weight and the thickness. That is, unlike carbon paper and carbon felt, a carbon fiber woven fabric has a specific property that, while it may become a material having optimum characteristics for a gas diffusion layer base material, it easily results adversely, depending on the weave thereof. With such a specific property utilized, however, it is possible to control a carbon fiber woven fabric to obtain optimum characteristics for a gas diffusion layer base material.

[0006]

A typical gas diffusion layer is produced, for example, in such a manner that a coating for formation of a water repellent layer, prepared by dispersing carbon black and a fluorocarbon resin in water, is applied onto one side of a base material to form a water repellent conductive layer



(hereinafter referred to as water repellent layer). In this case, in addition to the properties of the coating and a method for applying the coating onto the base material, the properties of the base material surface significantly control the state of the water repellent layer formation.

[0007]

Water repellency required for this water repellent layer also differs depending on the operating condition of the fuel cell. When the cell is operated under a high humidification condition, it is preferable that the water repellency of the outermost surface of the gas diffusion layer in contact with the catalyst layer be not very high. When the cell is operated under a low humidification condition, it is preferable that the aforementioned water repellency be high. That is to say, in the case where the outermost surface of the catalyst-layer-contacting-side of the gas diffusion layer has strong water repellency, there occurs a strong action of confining water within the electrode even when the polymer electrolyte membrane is in a sufficiently humidified state.

[0008]

In operation under a high humidification condition where a great amount of water is supplied from the outside, the aforementioned water repellency may be low since there is little need for the effect of confining water. In operation under a low humidification condition where a small amount of water is supplied from the outside, on the other hand, the

aforementioned water repellency is preferably increased. Especially in operation under a high humidification condition, it is important to form a water repellent layer (hereinafter referred to as uniform water repellent layer), in which not only the strength of the aforementioned water repellency of the outermost surface is controlled, but also the water repellency is gradually attenuated with a consecutive gradient or slope, from the catalyst-layer-contacting-side of the outermost surface of the gas diffusion layer to the separator-side-contacting side thereof. This permits smooth discharge of excess water, which is kept produced due to the reaction of the cell in operation, to the gas-flow-channel-side, without clogging of the micropores within the gas diffusion layer with the excess water.

[0009]

As methods for varying water repellency of a water repellent layer typically conducted have been a method of varying a weight ratio between carbon black and a fluorocarbon resin in a water repellent layer, and a method of varying the thickness of the water repellent layer or an applied amount of a coating for forming a water repellent layer while keeping the aforementioned weight ratio unchanged. In these cases, however, direct application of the coating for forming a water repellent layer onto a carbon fiber woven fabric would result in priority infiltration of the coating into a portion of the base material having a low fiber density, and it is therefore

difficult to uniformly apply the coating.

[0010]

Occurrence of such non-uniform infiltration of the coating would lead to formation of a non-uniform water repellent layer within the gas diffusion layer, where portions with strong water repellency and portions with weak water repellency exist at random. The opening between the portions with strong water repellency is apt to trap water therein, and the water once trapped is not readily discharged. In other words, due to the occurrence of non-uniform infiltration of the coating, as described above, it would become impossible to form a uniform water repellent layer, and thus impossible to effectively discharge excess water. Because non-uniform infiltration of a coating into a base material would significantly impair water permeability of a gas diffusion layer, accordingly, it is important particularly in a fuel cell operated under a high humidification condition to inhibit such non-uniform infiltration and form a uniform water repellent layer.

[0011]

A method as a countermeasure is under study which comprises previously applying a coating onto a different sheet to form a water repellent layer and then transfer-printing the resultant water repellent layer onto a gas diffusion layer base material made of carbon. This transfer-printing method however has a drawback that the number of processing steps

increases. Further, although inhibition of the aforementioned infiltration by the use of a coating for forming a water repellent layer, which is prepared to have a suitably high degree of viscosity, has been considered, there has not been obtained a sufficient inhibiting effect.

[0012]

Furthermore, because a conventional carbon fiber woven fabric for use as a gas diffusion layer base material has concave portions and convex portions with a large surface level, a problem exists in that a large number of openings are formed in a junction between a catalyst layer and a gas diffusion layer. The openings may become clogged with water during operation of the PEFC, thereby deteriorating the diffusibility of water. As thus described, in a PEFC operated under a high humidification condition, despite the possibility that the use of a carbon fiber woven fabric as a gas diffusion layer base material may control the carbon fiber woven fabric to have the optimum characteristics for the gas diffusion layer base material, such optimization has not currently been carried out.

[0013]

[Problem That the Invention Is to Solve]

With the aim of solving the aforementioned problems with the conventional PEFC, especially with the gas diffusion layer therein, an object of the present invention is to provide an MEA suitable for operation under a high

humidification condition by smoothing the surface of a carbon fiber woven fabric to be used as a gas diffusion layer base material, and further optimizing the surface so as to form thereon a uniform water repellent layer in which non-uniform infiltration of a coating for forming a water repellent layer is inhibited.

[0014]

[Means for Solving the Problem]

An electrolyte membrane-electrode assembly for fuel cells in accordance with the present invention comprises a polymer electrolyte membrane and a pair of electrodes with the polymer electrolyte membrane interposed therebetween, wherein each of the electrodes comprises a catalyst layer in contact with the polymer electrolyte membrane and a gas diffusion layer which has a water repellent layer in contact with the catalyst layer, the base material of the gas diffusion layer is made of a carbon fiber woven fabric, and the relationship:  $1/1500 \leq (10/W-Y)(10/Z-X)/XY \leq 1/5$  is satisfied when the carbon fiber woven fabric has a warp density of Z threads/cm, a weft density of W threads/cm, a warp thickness of X mm and a weft thickness of Y mm.

[0015]

It is preferable that the carbon fiber woven fabric have a thickness in the range of 0.05 mm to 0.3 mm. It is preferable that the carbon fiber woven fabric have a density in the range of 0.32 g/cc to 0.42 g/cc. It is further

preferable that one of the warp density and the weft density of the carbon fiber woven fabric be in the range of 16 threads/cm to 45 threads/cm, and the other of the two densities be in the range of 12 threads/cm to 40 threads/cm.

[0016]

The present invention provides a method of operating a fuel cell which comprises the aforementioned electrolyte membrane-electrode assembly for fuel cells in accordance with the present invention, and generates electric power by providing a supply of a humidified fuel gas to the anode and a supply of a humidified oxidant gas to the cathode, comprising a step of controlling the dew point of the fuel gas and the dew point of the oxidant gas to temperatures equivalent to, or 5 °C or less lower than, the temperature of the electrolyte membrane-electrode assembly in operation.

[0017]

[Mode for Embodying the Invention]

The present invention enables provision of an MEA suitable for operation under a high humidification condition by controlling a fabric construction of a carbon fiber woven fabric to be used as gas diffusion layer base material in a PEFC, so as to optimize the surface condition of the carbon fiber woven fabric, and a condition for applying a coating for forming a water repellent layer onto the carbon fiber woven fabric. The carbon fiber woven fabric to be used for the MEA of the present invention is characterized in that the

relationship:  $1/1500 \leq (10/W-Y)(10/Z-X)/XY \leq 1/5$  is satisfied when the carbon fiber woven fabric has a warp density of Z threads/cm, a weft density of W threads/cm, a warp thickness of X mm and a weft thickness of Y mm.

[0018]

In the above relational expression,  $XY \text{ mm}^2$  corresponds to the area of portions where warp thread is crossing weft thread (hereinafter referred to as crossing portions), and  $(10/W-Y)(10/Z-X) \text{ mm}^2$  corresponds to the area of the opening portions where neither the warp thread nor the weft thread exists (hereinafter referred to as opening portions). Namely, the carbon fiber woven fabric of the present invention is characterized in that the area ratio of the opening portions to the crossing portions:  $(10/W-Y)(10/Z-X)/XY$  is not less than 1/1500 and not more than 1/5.

[0019]

In the present invention, the carbon fiber woven fabric to be used as the gas diffusion layer base material is formed of carbon fiber thread, and the most common fabric structure is a plain weave. Other than the plain weave used can be a carbon fiber woven fabric having a twill or satin weave structure. In each of these carbon fiber woven fabrics, warp threads and weft threads are regularly combined in a geometrical pattern. Namely, a carbon woven fiber fabric is constituted such that carbon fiber threads (warp threads or weft threads) of a first group, arranged mutually in parallel,

are sequentially combined at right angles with carbon fiber threads (weft threads or warp threads) of a second group in a prescribed method. The carbon fiber threads belonging to the second group are also kept mutually parallel, to constitute a fabric.

[0020]

Next, a fabric structure of a carbon fiber woven fabric will be described by taking a plain weave carbon fiber woven fabric for instance. FIG. 1 is a plan view of a plain carbon fiber woven fabric, in which equally spaced warp threads 1 are crossing equally spaced weft threads 2 at right angles. Other than the case that the warp threads 1 and the weft threads 2 are composed of a single thread, there is the case that these threads are composed of plural threads, such as twines made of at least two threads. Because the cross section of the warp thread 1 or the weft thread 2 is not necessarily circular in form, in the present invention, the thickness of the warp thread and the thickness of the weft thread represent the respective widths of the warp thread and the weft thread which are illustrated in the plan view of the carbon fiber woven fabric, for the sake of convenience.

[0021]

In the carbon fiber woven fabric of the present invention, the area of opening portions 4, where neither the warp thread 1 nor the weft thread 2 exists, is made smaller relative to the area of crossing portions 3, where the warp



thread 1 is crossing the weft thread 2, such that the ratio between the two areas is  $1/1500$  to  $1/5$ . Thereby, when a coating for forming a water repellent layer is applied onto the carbon fiber woven fabric, priority infiltration of the coating from the opening portions 4 is inhibited, allowing formation of a uniform water repellent layer. This makes it possible to obtain a gas diffusion layer having a characteristic that water repellency is gradually attenuated with a gentle slope or gradient, from the catalyst-layer-contacting-side of the surface through the gas-flow-channel-side of the surface. The use of an MEA comprising such a gas diffusion layer enables smooth discharge of excess water into gas flow channels even in operation under a high humidification condition, with no water trapped into micropores within the gas diffusion layer.

[0022]

A problem having hitherto been raised is that when plural MEAs are stacked and then cramped to constitute a PEFC, increasing the cramping pressure to reduce the contact resistance between constituents would cause deflection of the constituents. To avoid this required is keeping the cramping pressure low within a range that prevents gas leakage. With the low cramping pressure, openings are produced in the interface between the catalyst layer and the gas diffusion layer, along with concavities and convexities of the base material. Since those openings are apt to become clogged with

water, excess water is not discharged out of the MEAs.

[0023]

According to the present invention, by increasing the area ratio of the crossing portions 3 of the carbon fiber woven fabric, the surface level difference between the concave portions and convex portions is reduced and the surface is thus smoothed. This can solve the aforementioned problem. That is, the carbon fiber woven fabric of the present invention has a surface with a small level difference between concave portions and convex portions because the area of crossing portions 3 having a larger thickness is 5 to 1500 times as large as the area of opening portions 4 having a smaller thickness. The use of this carbon fiber woven fabric can prevent the aforementioned formation of openings in the interface between the catalyst layer and the gas diffusion layer, whereby the problem of the clogging with excess water can be dissolved.

[0024]

As thus described, a PEFC using the MEA in accordance with the present invention, which comprises a gas diffusion layer where a uniform water repellent layer is formed on a carbon fiber woven fabric having a smooth surface, can exert high performance in operation under a high humidification condition which in particular requires the gas diffusion layer to have discharge capacity of excess water.

[0025]

In a carbon fiber woven fabric as a gas diffusion layer base material, when an area ratio of opening portions to crossing portions exceeds  $1/5$ , the surface thereof becomes insufficiently smooth. Further, it becomes impossible to sufficiently inhibit non-uniform infiltration of a coating. When the area ratio is below  $1/1500$ , meanwhile, pores within the gas diffusion layer are too small to provide sufficient gas diffusibility and water permeability.

[0026]

The carbon fiber woven fabric to be used for the MEA of the present invention has a thickness that is preferably in the range of 0.05 mm to 0.30 mm, and more preferably in the range 0.05 mm to 0.20 mm. Reduction of the thickness of the carbon fiber woven fabric can make the level difference between the concave portions and convex portions on the surface thereof smaller and the surface smoother. It is thereby possible to more effectively prevent the junction between the gas diffusion layer and the catalyst layer from being clogged with water, so that an MEA capable of more effectively preventing occurrence of the flooding phenomenon in operation under a high humidification condition can be provided.

[0027]

The thinner a carbon fiber woven fabric is made, the smaller a volume of openings within a gas diffusion layer and the smaller the amount of water staying within the gas

diffusion layer, and hence, such water can be readily discharged. For a carbon fiber woven fabric having a thickness less than 0.05 mm, however, it often happens that the handling thereof is difficult or the carbon fiber woven fabric cannot be woven because of insufficient tensile strength of the carbon fiber thread as the raw material thereof. As for a carbon fiber woven fabric having a thickness over 0.30 mm, on the other hand, there tends to occur a negative effect that a level difference between concave portions and convex portions on the surface of the carbon fiber woven fabric increases, causing the junction between the gas diffusion layer and the catalyst layer to be clogged with water.

[0028]

It is preferable that the carbon fiber woven fabric for use in the MEA of the present invention have a density in the range of 0.32 g/cc to 0.42 g/cc. With the fabric density of the carbon fiber woven fabric kept low, the carbon fiber woven fabric is compressed by pressure applied at the time of cramping the stacked fuel cell, and it thus becomes easier to smooth the surface thereof.

[0029]

In such a manner, with the carbon fiber woven fabric compressed for smoothing, the level difference between the convex portions and concave portions becomes smaller to allow elimination of openings, which may be clogged with water, from

the junction of the gas diffusion layer and the catalyst layer. As a result, there can be provided an MEA capable of more effectively preventing the flooding phenomenon in operation under a high humidification condition. The lower the density of the carbon fiber woven fabric is, the larger the above effect is. However, when a carbon fiber woven fabric has a density smaller than 0.32 g/cc, the mechanical strength of the carbon fiber woven fabric is so low that it becomes difficult to handle the carbon fiber woven fabric in production of an MEA. When a carbon fiber woven fabric has a density larger than 0.42 g/cc, on the other hand, the carbon fiber woven fabric is not sufficiently smoothed by pressure applied in the aforementioned cramping, making it impossible to sufficiently obtain the aforementioned effect.

[0030]

In the carbon fiber woven fabric for use in the MEA of the present invention, it is preferable that one of the warp density and the weft density be in the range of 16 threads/cm to 45 threads/cm, and the other thereof be in the range of 12 threads/cm to 40 threads/cm. By increasing the thread density (the number of threads of a carbon fiber woven fabric per unit length or width), the thickness per one thread is made smaller, and it is therefore possible to reduce the thickness of the crossing portions, and to thereby decrease the level difference between the convex portions and concave portions on the carbon fiber woven fabric surface. This leads

to a still smoother surface of the carbon fiber woven fabric and further permits formation of a uniform water repellent layer.

[0031]

Moreover, increasing the thread density may make a many opening portions existent in the carbon fiber woven fabric and the respective opening portion areas smaller. It is thereby possible to form a large number of fine spaces suitable for smoothly discharging excess water out of the MEA through the gas diffusion layer, or for dispersing the reaction gas within the gas diffusion layer. These effects bring about the smooth discharge of excess water in operation under a high humidification condition, thereby allowing provision of an MEA capable of more effectively preventing occurrence of the flooding phenomenon.

[0032]

The higher the warp density and the weft density of the carbon fiber woven fabric, the more significantly the above effect can be obtained. However, in the case where a carbon fiber woven fabric has a density beyond the aforementioned favorable range, the thread is so thin that it becomes difficult to weave and the carbon fiber woven fabric becomes difficult to handle. In the case where a carbon fiber woven fabric has a density below the aforementioned favorable range, on the other hand, the thread is so thick as to cause an increase in level difference between the convex portions

and concave portions on the carbon fiber woven fabric surface. When an MEA is produced using this carbon fiber woven fabric, openings which may be clogged with water tend to be formed in the junction between the catalyst layer and the gas diffusion layer.

[0033]

As the water repellent material to be included in the water repellent layer, a fluorocarbon resin, such as polytetrafluoroethylene (PTFE), is commonly used due to the excellent thermal resistance, acid resistance and chemical resistance thereof; silicone types and other water repellent materials capable of securing water repellency for a long period of time can also be used. Because the water repellent layer is formed on one side of the gas diffusion layer, which functions as a current collector, and is thus required to have electron conductivity, it is necessary that an electron conductive material be included in the water repellent layer.

[0034]

As the electron conductive material, carbons are generally used due to the excellent acid resistance properties thereof, and among them, acetylene black having strong water repellency is primarily used. Since it is difficult to produce a coating from a carbon having strong water repellency, however, there are cases where Ketjen black, which is a hydrophilic carbon, is more preferably used, depending on how to combine with the water repellent material. As other

electron conductive materials used can be metal materials. A typical method of forming a water repellent layer is directly applying a coating for forming a water repellent layer, prepared by dispersing the above water repellent material and electron conductive material in a dispersing medium such as water, onto one side of the carbon fiber woven fabric. The application method may be any of the spraying, spin coating, doctor blading, screen printing, coater applying and gravure printing methods.

[0035]

As the gas flow channel to be formed in the separator plate, there are; a straight-type gas flow channel which comprises plural straight paths arranged in parallel with each other in one direction from the inlet to the outlet thereof; a serpentine-type gas flow channel which comprises single or plural paths arranged to travel in a serpentine line; and so on. Shapes of gas flow channel are classified into crossing-type, facing-type and parallel-type, depending on the difference in the directions of the flowing gasses at the anode side and the cathode side. The present invention can be effectively applied to a PEFC comprising any of the aforementioned types of gas flow channels.

[0036]

The present invention provides a method of operating a PEFC which comprises the MEA in accordance with the present invention and a pair of separator plates having the gas flow



channels in contact with the external side of the MEA, wherein a dew point of a fuel gas, a dew point of an oxidant gas and the temperature of the MEA in operation are controlled within prescribed temperature ranges.

[0037]

The MEA of the present invention comprises the gas diffusion layer in which a uniform water repellent layer, free from non-uniform infiltration of the coating for forming a water repellent layer, is formed on the carbon fiber woven fabric with a smooth surface, as thus described. Thereby, the MEA in accordance with the present invention has sufficient dischargibility of excess water and diffusibility of a gas, as required for operation under a high humidification condition of a PEFC. The PEFC comprising this MEA therefore demonstrates an excellent performance especially when operated under the most typical high humidification condition, i.e. when under the condition that the dew point of the fuel gas to be supplied to the anode, the dew point of the oxidant gas to be supplied to the cathode, and the temperature of the MEA in operation are all controlled to the same temperature. In that case, by controlling the dew point of the fuel gas and the dew point of the oxidant gas to temperatures 5°C or less lower than the temperature of the electrolyte membrane-electrode assembly in operation, excellent performance, according to the case of equalizing the aforementioned dew points and temperature, can practically be obtained.

[0038]

[Working Examples]

Next, the present invention will be described more specifically by way of examples. In each of the examples and comparative examples, a unit cell was fabricated in a below-described method. FIG. 2 shows the representative view of those unit cells. Onto one side of a plain carbon fiber woven fabric prepared in each example and each comparative example, a coating for forming a water repellent layer was applied by doctor blading. The coating for forming a water repellent layer was prepared in such a manner that: acetylene black (AB) was mixed with water at a weight ratio of 1:4, the resultant mixture was added with a small amount of surfactant to be kneaded, which was then added to a PTFE dispersion (D1 manufactured by DAIKIN INDUSTRIES, LTD.) such that the weight ratio of the PTFE solid content to AB was 1:7. The carbon fiber woven fabric with this coating applied onto one side thereof was dried at about 100 °C for one hour, and then baked at about 270 °C for one hour, to produce a gas diffusion layer 13 in which a water repellent layer was formed on the carbon fiber woven fabric.

[0039]

Meanwhile, a catalyst layer 12 was attached by transfer printing onto each side of a polymer electrolyte membrane 11 (Nafion 112 manufactured by Du Pont, USA), comprising a perfluorosulfonic acid resin, except for the

periphery thereof. Subsequently, each of the gas diffusion layers 13 was attached to each of the catalyst layers 12 such that the water-repellent-layer-side of the gas diffusion layer 13 was in contact with the outer surface of the catalyst layer 12, to produce an MEA 15. The catalyst layer 12 to be transfer-printed onto the polymer electrolyte membrane 11 was formed by applying a catalyst paste onto a resin sheet, followed by drying. The area of the catalyst layer 12 in the MEA was 25 cm<sup>2</sup>. The paste for catalyst was prepared in such a manner that: 100 parts by weight of a catalyst obtained by carrying a platinum catalyst on a carbon fine powder (Ketjen Black EC, manufactured by LION CORPORATION) at a weight ratio of 1:1 was mixed with 80 parts by weight of a perfluorosulfonic acid resin dispersed in ethanol, and the obtained mixture was introduced into a mixed dispersing medium of water and ethanol, followed by stirring.

[0040]

Next, a gasket 18 was then disposed on each side of the polymer electrolyte membrane 11 on the periphery of the MEA 15, which was hot pressed at 100°C for 5 minutes for attachment. The resultant assembly was sandwiched from one side thereof by a cathode-side carbon-made separator plate 17 and from another side by an anode-side carbon-made separator plate 17, and they were cramped such that a surface pressure of about 7 kgf/cm<sup>2</sup> was applied to ribs 19 formed on the separator plates 17, to fabricate a unit cell of a PEFC. The

cathode-side and anode-side separator plates 17 were each provided with serpentine-type gas flowing channels 16 comprising three grooves with a cross-sectional area of 1.0 cm<sup>2</sup>.

[0041]

The thicknesses of the warp thread and the weft thread of the carbon fiber woven fabric used in each example and each comparative example were measured by means of an SEM photograph at a magnification of 100 times taken with an accelerating voltage of 15 kV. The number of threads per 1 cm (warp thread density and weft thread density) was calculated by measuring the number of threads per 5 cm in a micrograph at a magnification of 25 times and then calculating an average value per 1 cm from the above measured value. The carbon fiber woven fabric was punched out into a size of 12 cm × 12 cm and the weight thereof was measured, from which the basis weight of the carbon fiber woven fabric was calculated. The density of the carbon fiber woven fabric was determined from the above-calculated basis weight and the thickness thereof.

[0042]

《Example 1》

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.48 mm comprising a twine and weft threads with a thickness of 0.48 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread

density of 20.1 threads/cm, a weft thread density of 18.1 threads/cm, a basis weight of 110 g/m<sup>2</sup>, a thickness of 0.28 mm and a density of 0.393 g/cc.

[0043]

«Example 2»

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.45 mm comprising a twine and weft threads with a thickness of 0.45 mm comprising a single yarn, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 17.7 threads/cm, a weft thread density of 15.4 threads/cm, a basis weight of 105 g/m<sup>2</sup>, a thickness of 0.29 mm and a density of 0.362 g/cc.

[0044]

«Example 3»

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.445 mm comprising a twine and weft threads with a thickness of 0.445 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 15.7 threads/cm, a weft thread density of 15.4 threads/cm, a basis weight of 80 g/m<sup>2</sup>, a thickness of 0.20 mm and a density of 0.400 g/cc.

[0045]

«Example 4»

A carbon fiber woven fabric, woven by warp threads

with a thickness of 0.36 mm comprising a twine and weft threads with a thickness of 0.36 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 23.6 threads/cm, a weft thread density of 22.00 threads/cm, a basis weight of 115 g/m<sup>2</sup>, a thickness of 0.29 mm and a density of 0.397 g/cc.

[0046]

«Example 5»

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.465 mm comprising a twine and weft threads with a thickness of 0.47 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 21.3 threads/cm, a weft thread density of 20.1 threads/cm, a basis weight of 125 g/m<sup>2</sup>, a thickness of 0.30 mm and a density of 0.417 g/cc.

[0047]

«Comparative Example 1»

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.42 mm comprising a twine and weft threads with a thickness of 0.42 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 15.7 threads/cm, a weft thread density of 15.7 threads/cm, a basis weight of 114 g/m<sup>2</sup>, a thickness of 0.30 mm

and a density of 0.380 g/cc.

[0048]

«Comparative Example 2»

A carbon fiber woven fabric, woven by warp threads with a thickness of 0.47 mm comprising a twine and weft threads with a thickness of 0.47 mm comprising a twine, was used as a gas diffusion layer base material to fabricate a unit cell. The carbon fiber woven fabric had a warp thread density of 21.3 threads/cm, a weft thread density of 17.3 threads/cm, a basis weight of 100 g/m<sup>2</sup>, a thickness of 0.27 mm and a density of 0.370 g/cc.

[0049]

A variety of cell tests were conducted in a below-described procedure, using the unit cells in Examples 1 to 5 and Comparative Examples 1 and 2, where a variety of carbon fiber woven fabrics were produced by varying the weaves thereof as thus described. First, a fuel gas (hydrogen gas) heated and humidified so as to have a dew point of 70°C and an oxidant gas (air) heated and humidified so as to have a dew point of 70°C were respectively supplied to the anode and the cathode, and a cell test 1 was conducted under conditions that the temperature of the MEA in operation was 70°C, a hydrogen gas utilization rate was 70% and an air utilization rate was 40%. Subsequently, the air utilization rate was varied from 40% to 80%, and then a battery test 2 was conducted.

[0050]

Next, a cell test 3 was conducted under conditions that the dew point of the hydrogen gas to be supplied to the anode was 67°C, the dew point of the air to be supplied to the cathode was 70°C, the temperature of the MEA in operation was 70°C, a fuel gas utilization rate was 70% and an air utilization rate was 40%. Subsequently, the air utilization rate was varied from 40% to 80%, and then a battery test 4 was conducted.

[0051]

A cell test 5 was conducted under conditions that the dew point of the hydrogen gas to be supplied to the anode was 67°C, the dew point of the air to be supplied to the cathode was 65°C, the temperature of the MEA in operation was 70°C, a fuel gas utilization rate was 70% and an air utilization rate was 40%. Subsequently, the air utilization rate was varied from 40% to 80%, and then a battery test 6 was conducted.

[0052]

A cell test 7 was conducted under conditions that the dew point of the hydrogen gas to be supplied to the anode was 65°C, the dew point of the air to be supplied to the cathode was 65°C, the temperature of the MEA in operation was 70°C, a fuel gas utilization rate was 70% and an air utilization rate was 40%. Subsequently, the air utilization rate was varied from 40% to 80%, and then a battery test 8 was conducted.



[0053]

A cell test 9 was conducted under conditions that the dew point of the hydrogen gas to be supplied to the anode was 65°C, the dew point of the air to be supplied to the cathode was 55°C, the temperature of the MEA in operation was 70°C, a fuel gas utilization rate was 70% and an air utilization rate was 40%. Subsequently, the air utilization rate was varied from 40% to 80%, and then a battery test 10 was conducted. A current density during the operation was 0.3 A/cm<sup>2</sup> in any of the above cell tests 1 to 10.

[0054]

Table 1 shows the respective area ratios of the opening portions to the crossing portions: (10/W-Y)(10/Z-X)/XY of the carbon fiber woven fabrics used in Examples 1 to 5 and Comparative Examples 1 and 2, and the respective operating voltage values in the cell tests 1 to 10. In Table 1, the aforementioned area ratio is simply represented by "area ratio" as a matter of convenience.

[0055]

Table 1

	Ex.1	Ex.2	Ex.3	Ex.4	Ex.5	Com.Ex.1	Com.Ex.2
Area ratio	1/177	1/9	1/5	1/22	1/1449	1/4	1/5560
*A	0.731	0.729	0.726	0.730	0.736	0.718	0.621
*B	0.719	0.715	0.712	0.715	0.727	0.658	0.405
A-B(V)	0.012	0.014	0.014	0.015	0.009	0.060	0.216
*C	0.727	0.721	0.718	0.724	0.732	0.708	0.633
*D	0.718	0.714	0.709	0.711	0.726	0.688	0.477
C-D(V)	0.009	0.007	0.009	0.013	0.006	0.020	0.156
*E	0.724	0.709	0.701	0.712	0.728	0.680	0.662
*F	0.718	0.708	0.700	0.710	0.727	0.665	0.583
E-F(V)	0.006	0.001	0.001	0.002	0.001	0.015	0.079
*G	0.724	0.700	0.698	0.709	0.728	0.651	0.676
*H	0.717	0.688	0.684	0.704	0.726	0.648	0.621
G-H(V)	0.007	0.002	0.005	0.005	0.002	0.003	0.055
*I	0.712	0.663	0.637	0.687	0.724	0.610	0.723
*J	0.716	0.681	0.659	0.698	0.724	0.643	0.722
I-J(V)	-	-	-	-	0.000	-0.033	0.001
	0.004	0.018	0.022	0.011			

\*A: Operating voltage(V) in cell test 1

\*B: Operating voltage(V) in cell test 2

\*C: Operating voltage(V) in cell test 3

\*D: Operating voltage(V) in cell test 4

\*E: Operating voltage(V) in cell test 5

\*F: Operating voltage(V) in cell test 6

\*G: Operating voltage(V) in cell test 7

\*H: Operating voltage(V) in cell test 8

\*I: Operating voltage(V) in cell test 9

\*J: Operating voltage(V) in cell test 10

[0056]

The result that differences (A-B, C-D, E-F, G-H and I-J) in operating voltage in the case of varying the air utilization rate from 40% to 80% under the same conditions of

the reaction gas humidification and of the MEA temperature during the operation are positive values reveals that the operating voltage at the utilization rate of 40% is higher than the operating voltage at the utilization rate of 80%. The result that those differences are small shows that the voltage variation due to the utilization rate (flow rate) of the air to be supplied to the cathode is small so that stable output can be obtained during the operation. On the other hand, the result that the aforementioned differences in operating voltage are large indicates that: the operating voltage is apt to vary due to the flow rate of the air; and when the flow rate of the air is lowered, the operation tends to be in a flooding state. Further, the result that the aforementioned differences in operating voltage are negative values reveals that the operation tends to be in somewhat of a dry state when the flow rate is raised because the voltage value increases as the flow rate is lowered.

[0057]

As understood from Table 1, the unit cells in Examples 1 to 5, using the carbon fiber woven fabrics with the area ratio:  $(10/W-Y)(10-Z-X)/XY$  in the range of 1/1500 to 1/5, exhibited higher operating voltages in any of the cell tests 1 to 8 than the operating voltages of the unit cells in Comparative examples 1 and 2, because excess water in the operation under a high humidification condition in Examples 1 to 5 was smoothly discharged.

[0058]

On the other hand, as compared with the unit cells in Examples, the unit cells in Comparative Examples 1 and 2, using the carbon fiber woven fabric with the area ratio:  $(10/W-Y)(10-Z-X)/XY$  out of the aforementioned range, exhibited lower operating voltages in any of the cell tests 1 to 6, and larger differences (A-B, C-D and E-F) in operating voltage due to the difference in utilization rate (flow rate) of the air. This is presumably because water produced at the cathode was not smoothly discharged to induce the flooding.

[0059]

More specifically, it is presumed that in Comparative Example 1, a uniform water repellent layer was not formed because there were too many opening portions in the carbon fiber woven fabric, and excess water was not smoothly discharged because the level difference between the convex portions and concave portions on the surface was large. It is thought on the contrary that in Comparative Example 2, the excess water was not smoothly discharged because there were few opening portions in the carbon fiber woven fabric, thereby making it difficult for excess water to penetrate through the gas diffusion layer.

[0060]

In any of Examples 1 to 5 and Comparative Example 1, the operating voltages observed in the cell tests 9 and 10 are smaller than in the cell tests 1 to 8. Moreover, the result

that the differences in operating voltage (I-J) of these unit cells are either minus values or zero indicates that the operation tends to be in somewhat of a dry state when an air at a relatively low humidity, a dew point of 55°C, is supplied to the cathode. Meanwhile, For Comparative Example 2, since penetration of water through the gas diffusion layer is difficult, the operation does not tend to be in a dry state and the operating voltage difference (I-J) is a positive value even in the cell tests 9 and 10.

[0061]

[Effects of the Invention]

According to the present invention, there can be provided an electrolyte membrane-electrode assembly for polymer electrolyte fuel cells, which has an excellent flooding-resistance characteristic in operation under a high humidification condition, and can obtain a high operating voltage.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1]

A plan view of a carbon fiber woven fabric in the present invention.

[FIG.2]

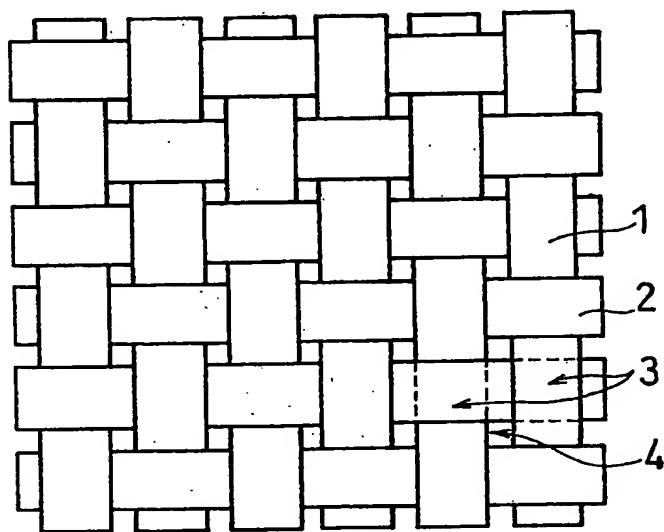
A vertical sectional view of a unit cell comprising an electrolyte membrane-electrode assembly in an example of the present invention.

[Explanation of Reference Numerals]

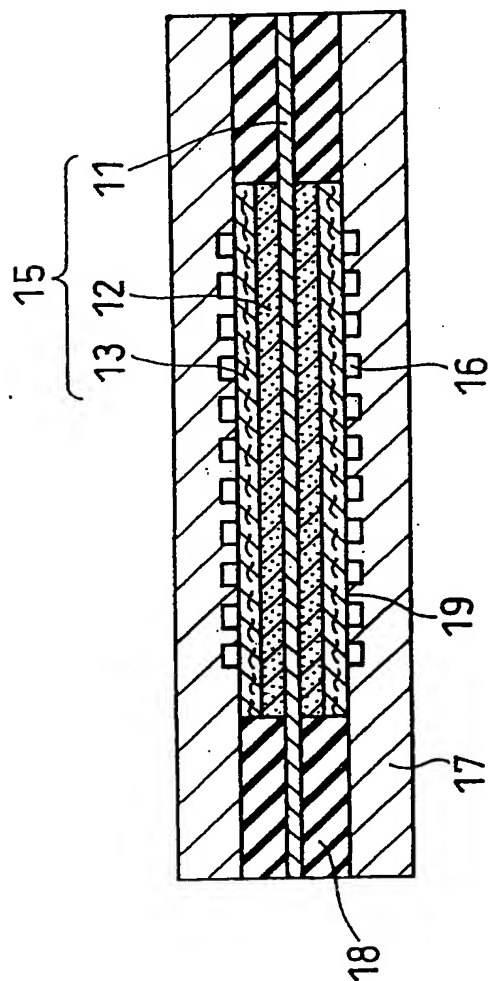
1. Warp thread
2. Weft thread
3. Portion where warp thread is crossing weft thread (Crossing portion)
4. Opening portion where neither warp thread nor weft thread exists (Opening portion)
11. Polymer electrolyte membrane
12. Catalyst layer
13. Gas diffusion layer
15. Electrolyte membrane-electrode assembly
16. Gas flowing channel
17. Separator plate
18. Gasket
19. Rib

【書類名】 図面 [DOCUMENT NAME] Drawings

【図1】 [FIG. 1]



【図2】 [FIG. 2]





2002-359314

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] With respect to a carbon fiber woven fabric to be used as a gas diffusion layer base material in a polymer electrolyte fuel cell, the surface thereof is smoothed and further optimized so as to inhibit non-uniform infiltration of a coating for forming a water repellent layer, to provide an electrolyte membrane-electrode assembly suitable for operation under a high humidification condition.

[SOLVING MEANS] As the gas diffusion layer base material used is a carbon fiber woven fabric, wherein a ratio of the area of opening portions where neither warp thread nor weft thread exists:  $(10/W-Y)(10/Z-X)$  to the area of portions where warp thread is crossing weft thread:  $XY \text{ mm}^2$  is in the range of  $1/1500$  to  $1/5$ , when the carbon fiber woven fabric has a warp density of  $Z$  threads/cm, a weft density of  $W$  threads/cm, a warp thickness of  $X$  mm and a weft thickness of  $Y$  mm.

[SELECTED DRAWING] FIG. 1